Preamble

Ceramics and polymer-ceramic composites associated with high dielectric constants are of both scientific and industrial interest as these could be used in devices such as capacitors, resonators and filters. High dielectric constant facilitates smaller capacitive components, thus offering the opportunity to miniaturize the electronic devices. Hence there is a continued interest on high dielectric constant materials over a wide range of temperatures. Recently, $CaCu_3Ti_4O_{12}$ (CCTO) ceramic which has centro-symmetric body centered cubic structure has attracted considerable attention due to its large dielectric constant ($\varepsilon \sim 10^4$-10^5) which is nearly independent of frequency (upto 10 MHz) and low thermal coefficient of permittivity (TCK) over 100-600K temperature range. Apart from the high dielectric ceramics, high dielectric polymer-ceramic composites have also become promising materials for capacitor applications. By combining the advantages of high dielectric ceramics and low leakage behaviour of polymers, one can fabricate new hybrid materials with high dielectric constants, and high breakdown field to achieve high volume efficiency and energy storage density for capacitor applications.

The CCTO polycrystalline powders were generally prepared by the conventional solid-solid reaction route with $CaCO_3$, TiO_2 and CuO as the starting materials. This method of preparation often requires high temperatures and longer durations. To overcome these difficulties, in the present investigations, an attempt has been made to synthesize CCTO by adopting microwave assisted heating technique and wet chemical synthesis routes. Also the CCTO crystallites (size varying from nano to micrometers) incorporated in the Polyvinyliden fluoride (PVDF) and Polyaniline (PANI) matrix and several composites with high dielectric constants were fabricated and investigated. Further, the high dielectric constant glasses in the system $(100\text{-}x)TeO_2\text{-}xCaCu_3Ti_4O_{12}$, (x=0.5 to 3) were fabricated by the conventional melt-quenching technique and their structural and dielectric properties were studied. The results obtained pertaining to these aforementioned investigations are classified as follows.

Chapter 1 is intended to give basic information pertaining to the dielectrics and various mechanisms associated with high dielectric constants. Brief exposure to the high dielectric constant materials is also given. The structural aspects of CCTO, various synthetic routes adopted for the synthesis and the origin of the dielectric anomaly in CCTO are elaborated. In addition, basic information about the high dielectric polymer-ceramic composites and glasses are provided.

In chapter 2 the various experimental techniques that were employed to synthesize and characterize the materials under investigation were discussed.

Chapter 3 reports the synthesis and characterization of $CaCu_3Ti_4O_{12}$, (CCTO) powders by microwave assisted heating at 2.45 GHz, 1.1kW. The processing and sintering were carried out at different temperatures for varied durations. The optimum calcination temperature using microwave heating was found to be 950^{o}C for 20 minutes to obtain cubic CCTO powders. This is found to be fast and energy efficient as compared to that of the conventional methods. The structure, morphology and dielectric properties of the CCTO ceramic processed by microwave assisted heating were studied via X-ray diffraction, Scanning electron microscopy (SEM) and impedance analyser. These studies revealed that, the microwave sintered (MS) samples were less porous than that of the conventional ones. Relative density of about 95% was achieved for the MS pellets (1000^{o}C/60min) while for the conventional sintered (CS) pellets (1100^{o}C/2h) it was only 91%. The dielectric constants for the microwave sintered (1000^{o}C/60min) ceramics were found to vary from 11000 to 6950 in the 100 Hz to 100 kHz frequency range. The presence of larger grains (6-10μm) in the MS samples contributed to the higher dielectric constants.

Chapter 4 deals with the synthesis of complex oxalate precursor, $CaCu_3(TiO)_4(C_2O_4)_8 \bullet 9H_2O$, by the wet chemical route. The various trials and the different reaction schemes involved for the preparation of complex oxalate precursor were highlighted. The oxalate precipitate thus obtained was characterized by the wet chemical analyses, X-ray diffraction, FTIR absorption and TG/DTA analyses.

The complex oxalate precursor, $CaCu_3(TiO)_4(C_2O_4)_8.9H_2O$ was subjected to thermal oxidative decomposition and the products of thermal decomposition were investigated employing XRD,TGA, DTA and FTIR techniques. Nanocrystallites of $CaCu_3Ti_4O_{12}$ with the size varying from 30-200 nm were obtained at a temperature as low as 680^{o}C. The nanocrystallites of $CaCu_3Ti_4O_{12}$ were characterized using Electron Spin Resonance (ESR) and optical reflectance techniques. The selected area electron diffraction (SAED) pattern with the zone axis [012] and spot pattern in electron diffraction (ED) indicate their single-crystalline nature. The optical reflectance and ESR spectra indicate that the Cu (II) coordination changes from distorted octahedra to nearly flattened tetrahedra (squashed) to square planar geometry with increasing heat treatment temperature. The powders derived from the oxalate precursor have excellent sinterability resulting in high density ceramics which exhibited giant dielectric constants upto 40,000 (1 kHz) at 25^{o}C, accompanied by low dielectric loss < 0.07.

The effect of calcium content on the dielectric properties of $Ca_xCu_3Ti_4O_{12}$ (x=0.90, 0.97, 1.0, 1.1 and 1.15) derived from the oxalate route was described in **Chapter 5**. The structural, morphological and dielectric properties of the ceramics were studied using X-ray diffraction, Scanning Electron Microscope along with Energy Dispersive X-ray Analysis (EDX), and Impedance analyzer. The X-ray diffraction patterns obtained for the x= 0.97, 1.0 and 1.1 ceramics could be indexed to a body–centered cubic perovskite related structure associated with the space group Im3. The microstructural studies revealed that the grains are surrounded by exfoliated sheets of Cu-rich phase. The microstructure that is evolved for the $Ca_{0.97}$ ceramic more or less resembles that of the $Ca_{1.0}$ ceramic, but the density of such exfoliated sheets of cu-rich phase is lesser for the $Ca_{0.97}$ ceramic and none for $Ca_{1.1}$ ceramic. The sintered pellet (x=0.97) was ground and thinned to the required thickness (~ 20nm) and analyzed using Transmission Electron Microscopy (TEM). The current-voltage (I-V) characteristics of the ceramics exhibited non-linear behaviour. The dielectric properties of these suggest that the sample corresponding to the composition x=0.97, has a reduced dielectric loss while retaining its high dielectric constant.

Chapter 6 illustrates the results concerning the fabrication and characterization of nanocrystal composites of Polyaniline (PANI) and $CaCu_3Ti_4O_{12}$ (CCTO). These were prepared using a simple procedure involving in-situ polymerization of aniline in dil. HCl. The PANI and the PANI-CCTO composites were subjected to X-ray diffraction, Fourier Transform Infrared (FTIR), Thermo gravimetric, Scanning Electron Microscopic (SEM) and Transmission electron microscopic analyses. The FTIR spectra recorded for the composites was similar to that of pure PANI unlike in the case of X-ray diffraction wherein the characteristics of both PANI and CCTO were reflected. The TGA in essence indicated the composites to have better thermal stability than that of pure PANI. The composite corresponding to 50%CCTO-50%PANI exhibited higher dielectric constant ($4.6 x 10^6$ @100Hz). The presence of the nano crystallites of CCTO embedded in the nanofibers of PANI matrix was established by TEM. The AC conductivity increased slightly upto 2kHz as the CCTO content increased in the PANI which was attributed to the polarization of the charge carriers. The value of dielectric constant obtained was higher than that of the other PANI based composites reported in the literature.

Chapter 7 deals with the fabrication and characterization of diphasic Poly(vinylidene fluoride) (PVDF)-CCTO composite. The CCTO crystallites (size varying from nano to micrometers) incorporated in the Polyvinylidene fluoride (PVDF) and composites with varying CCTO content were fabricated. The structural, morphological and dielectric properties of the composites were studied using X-ray diffraction, Thermal analysis, Scanning Electron Microscope (SEM), Transmission Electron Microscopic (TEM) and Impedance analyzer. The room temperature dielectric constant as high as 95 at 100Hz has been realized for the composite with 0.55 Vol.fraction of CCTO (micro sized crystallites), which has increased to about 190 at 150^{o}C. Whereas, the PVDF/CCTO nanocrystal composite with 0.13Vol.fraction of CCTO has exhibited higher room temperature dielectric constant (90 at 100Hz). The PVDF/CCTO nanocrystal composite was further investigated for the breakdown strength and electric modulus. The breakdown strength plotted against the dielectric constant evidenced an inverse relationship of breakdown voltage with the dielectric constant. The relaxation processes associated with these composites were attributed to the interfacial polarization or Maxwell-Wagner-Sillars (MWS) effect. Various theoretical models were employed to rationalize the dielectric behavior of these composites.

The fabrication and characterization details of optically clear colored glasses in the system (100-x)TeO_2-x$CaCu_3Ti_4O_{12}$, (x=0.5 to 3 mol%) are reported in **Chapter 8**. The color varies from olive green to brown as the $CaCu_3Ti_4O_{12}$ (CCTO) content increased in TeO_2 matrix. The X-ray powder diffraction and differential scanning calorimetric analyses that were carried out on the as-quenched samples confirmed their amorphous and glassy nature respectively. The optical transmittance of the glasses exhibited typical band-pass filter characteristics. The dielectric constant and loss in the 100 Hz-1MHz frequency range were monitored as a function of temperature (323K-673K). The dielectric constant and the loss increased as the CCTO content increased in TeO_2 at all the frequencies and temperatures under study. Further, the dielectric constant and the loss were found to be frequency independent in the 323-473 K temperature range. The value obtained for the loss at 1MHz was 0.0019 which was typical of low loss materials, and exhibited near constant loss (NCL) contribution to the ac conductivity in the 100Hz-1MHz frequency range. The electrical relaxation was rationalized using the electrical modulus formalism. These glasses are found to be more stable (a feature which may be of considerable interest) as substrates for high frequency circuit elements in conventional semiconductor industries.

Thesis ends with summary and conclusions, though each chapter is provided with conclusions and complete list of references.